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Electro-photocatalytic degradation of acid orange II using a novel TiO₂/ACF photoanode

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ABSTRACT

A novel photoanode was prepared by immobilizing TiO₂ film onto activated carbon fibers (TiO₂/ACF) using liquid phase deposition (LPD) to study the electro-photocatalytic (EPC) degradation of organic compounds exemplified by an azo-dye, namely, Acid Orange II (AOII). Results demonstrated that by applying a 0.5 V bias (vs. SCE) across the TiO₂/ACF electrode, the AOII degradation rate was increased significantly compared to that of photocatalytic (PC) oxidation. The application of an electric field promotes the separation of photogenerated electrons and holes as confirmed by electrochemical impedance spectroscopy (EIS) measurements. The structural and surface morphology of the TiO₂/ACF electrode was characterized by field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). SEM images showed that TiO₂ was deposited on almost every carbon fiber with an average thickness of about 200 nm with the inner space between neighboring fibers being maintained unfilled. The morphological features of the photo-anode facilitated the passage of solution as well as UV light through the felt-form electrode and created a three-dimensional environment favorable to EPC oxidation. Both the large outer surface area of the 3D electrode and the good organic adsorption capacity of the ACF support promoted high contact efficiency between AOII and TiO₂ surface. Anatase was the major crystalline TiO₂ deposited. UV-vis spectrophotometry, TOC (total organic carbon) analysis, and HPLC technique were used to monitor the concentration change of AOII and intermediates as to gain insight into the EPC degradation of AOII using the TiO₂/ACF electrode.

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1. Introduction

The degradation of organic pollutants in water by the photocatalytic semiconductor TiO₂ has attracted extensive attention in recent decades. Many researchers have reported that most refractory organic contaminants such as detergents,

dyes, pesticides, and herbicides, can be decomposed by TiO₂ under UV-light irradiation. It has been known also that conventional photooxidation has two major disadvantages: difficulty in solid-liquid separation and low photo-efficiency. For use in TiO₂ suspension, extra effort is needed to separate the photocatalytic TiO₂ particles from water. To deal with the

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problem of solid–liquid separation, fixed TiO_2 systems where nano-sized TiO_2 is immobilized onto solid surfaces such as glass (Addamo et al., 2008), ceramic membrane (Sabate et al., 1992), or steel plate (Takenori et al., 2000) has been suggested. Furthermore, conventional TiO_2 photocatalysis has relatively low quantum yield (less than 10% generally) due to rapid hole–electron recombination. A high degree of recombination between charge carriers is a waste of radiation energy, especially when artificial rather than natural light sources are used. Intuitively, efficient separation of charge carriers can be achieved using an electrochemically assisted photocatalytic system, in which an electrical bias is applied across the photoanode, while the photogenerated electrons on the semiconductor such as TiO_2 are pulling away from the photo-anode and fed to the cathode through an external electric circuit, thus inhibiting the hole–electron recombination. Immobilizing TiO_2 on a photo-node provides an ideal solution to the above technical deficiencies of conventional photocatalytic oxidation processes.

In many previous studies, photoanodes were generally prepared by coating TiO_2 on a traditional plate electrode such as conducting glass (e.g. ITO) or titanium sheet (Palombari et al., 2002; Jiang et al., 2004; Quan et al., 2004; Li et al., 2005). This configuration is a two-dimensional (2D) arrangement that provides only limited adsorption sites for the chemical contaminants which affect subsequent electrophotodegradation of the chemical in question, as the degradation process is directly proportional to the specific surface area of the photoelectrode available. A three-dimensional (3D) photoelectrode would be a better configuration than that of a 2-D electrode. Under this context, activated carbon fibers (ACF) are ideal material for making 3-D electrodes (Fan et al., 2006). ACF is a highly micro-porous material and has high specific surface area and large pore volume, which can facilitate the adsorption of organic chemicals.

The objectives of this study were to test the hypothesis that the application of bias potential across the photoanode can enhance the photocatalytic oxidation process and that a three-dimensional (3D) instead of a two-dimensional (2D) photoanode configuration would be much efficient in the electro-photocatalytic oxidation of organic compounds. In this study, a novel photoanode was prepared by incorporating nano- TiO_2 crystalline onto ACF. The electro-photocatalytic oxidation efficiency was assessed using Acid Orange II (AOII) as model organic contaminant. To the best of our knowledge, no such anode and its associated electro-photocatalytic characteristics have been reported in the literature.

2. Experimental

2.1. Titanium dioxide film deposition

Activated carbon fibers (ACF) in felt form (Xuesheng Technology Co. Ltd, Shandong Province, China), with a specific surface area of $1237 \text{ m}^2/\text{g}$, were used in this study. The ACF was pretreated in boiling water for 60 min, air-dried overnight, and then hydroxylated by immersion in 1 M of ammonium peroxydisulfate aqueous solution at 50°C for 60 min. The coating procedure, known as liquid phase deposition (LPD),

was adopted from Koumoto et al. (1999) and Herbig and Löbmann (2004). In order to test the integrity of the TiO_2 coating, the TiO_2/ACF so prepared was placed in 100 mL of deionized water in a glass bottle and shaken (side-wide) at 150 rpm for 12 h. The turbidity of the deionized water was then determined with a turbidimeter (HACH 2100N, USA). Results indicated that there was no significant increase in turbidity of the deionized water. Briefly, ammonium hexafluorotitanate ($(\text{NH}_4)_2\text{TiF}_6$ (AHFT), 1.176 g, C.P.) was dissolved in 84 mL of deionized water and mixed with 36 mL of boric acid (0.5 M, H_3BO_3 , A.R.) to form a solution containing 0.05 M of AHFT and 0.15 M of H_3BO_3 . The addition of 2 M of hydrochloric acid enabled the pH to be adjusted to 2.8 without significantly increasing the solution volume. The substrate, ACF, was vertically immersed in a freshly prepared deposition solution at 50°C for 6 h. Then the TiO_2 -coated ACF was removed from the solution, rinsed with deionized water, and air-dried overnight. Finally the samples were annealed at 350°C in nitrogen atmosphere for 180 min. In this study, the ACF loaded with TiO_2 film was designated as TiO_2/ACF . The amount of TiO_2 loading was estimated to be ~5 wt.%, which was determined from weight loss of the TiO_2/ACF after calcination at 700°C for 5 h in an air stream. (Note: it is expected that there is an optimal TiO_2 loading necessary for the maximum degree of organic degradation by the electro-photocatalytic oxidation process.) The final TiO_2/ACF electrode prepared was in the form of 3-mm felt. To compare the electro-photocatalytic efficiency of the 3D with that of the 2D photo-anode, another electrode was prepared by coating a thin film of TiO_2 on a titanium sheet (TiO_2/Ti) using the sol–gel method (Shang et al., 2003).

2.2. Material characterization

Surface characterization of TiO_2/ACF was carried out by scanning electron microscopy (JSM-6301F, field emission scanning electron microscope, FE-SEM). Crystal phases were identified by automatic X-ray diffractometer (XRD, Rigaku D/max-2500, Japan) with $\text{CuK}\alpha$ radiation operated at 40 kV and 20 mA.

2.3. Electro-photocatalytic degradation of Acid Orange II

Degradation of Acid Orange II (AOII) was performed in a quartz reactor ($35 \text{ mm} \times 35 \text{ mm} \times 70 \text{ mm}$). TiO_2/ACF (or TiO_2/Ti) was used as the photoanode with an effective working area of 12 cm^2 , which was placed at 2 cm away from a 15-w germicidal lamp (90% energy output at 253.7 nm). Pt wire, 72 mm in length with a diameter of 1.5 mm, was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The power source was an EG&G model 263A potentiostat (Princeton Applied Research, USA). Electrochemical impedance spectra (EIS) were recorded in the potentiostatic mode. The amplitude of the sinusoidal wave was 10 mV, and the frequency of the sinusoidal wave was in the range from 0.1 Hz to 100 kHz.

The initial concentration of the An AOII solution was 200 mg/L (in 0.01 M of sodium sulfate as supporting electrolyte). The solution was sampled periodically during reaction as to monitor the degree of AOII degradation by measuring

the absorbance at 484 nm using a UV–vis spectrophotometer (Hitachi U-3010, Japan). The UV–vis spectra of the samples were recorded also from 190 to 600 nm as to observe intermediates that may be detectable by UV–visible spectrophotometry. Total organic carbon (TOC) was measured with a Phoenix 8000 TOC analyzer (Tekmar-Dohrmann Co., USA).

Separate experiments were run to study the concentration change of AOII and its degradation products using a high-performance liquid chromatograph (HPLC, Hitachi L-2000, Japan). The initial concentration of AOII was 50 mg/L in 0.01 M of sodium sulfate as supporting electrolyte. Aliquots of sample (e.g., 20 μ L) were injected into the HPLC column running with the mobile phase of acetonitrile/water (0.025 M of ammonium acetate) at 35/65 (v/v). The separation was performed using an ODS-25u reversed phase column (Alltech, USA) at a flow rate of 1.0 mL/min and

column temperature of 40 °C. Most of the aromatic intermediates detected in this study had strong absorbance at around 254 nm, and thereafter a diode array detector was used to quantify the concentration of intermediates at this wavelength.

3. Results and discussion

3.1. SEM and XRD analysis of TiO_2/ACF

Fig. 1 shows typical SEM images of the TiO_2/ACF as well as the unmodified ACF for comparison. The surface of the unmodified carbon fiber is full of long shallow grooves [Fig. 1a and b]. As shown in Fig. 1c and d, continuous TiO_2 film was immobilized on almost every fiber of ACF. The

Fig. 1 – SEM images of the TiO_2/ACF and unmodified activated carbon fibers. (a) unmodified ACF at 500 $\times$; (b) single unmodified ACF at 5000 $\times$; (c) TiO_2/ACF at 500 $\times$; (d) single activated fiber coated with TiO_2 at 5000 $\times$; (e) TiO_2 coating at 50 000 $\times$; (f) cross-sectional view ACF with TiO_2 coating at 30 000 $\times$.

Fig. 2 – XRD spectra of the unmodified ACF and TiO_2/ACF .

small spherical particles, sparsely attached to the film surface, were produced from TiO_2 precipitation in solution. In spite of the high degree of TiO_2 coating on the fibers, the TiO_2/ACF retained the same spatial distribution as the unmodified ones; there were no adjacent fibers being connected to each other by the TiO_2 particles deposited. Thus, the large inner space between neighboring fibers created a 3-D environment that could enable the transport of chemical species in question and UV irradiation. This distinct feature (i.e., felt form) makes the TiO_2/ACF photoanode different from that of the plate type electrodes such as TiO_2/ITO and TiO_2/Ti , which can provide only limited two-dimensional surface for photodegradation. The image of the TiO_2 coating was further enlarged to show details of the morphology of its surface [Fig. 1e]. The coated TiO_2 layer did not form compact configuration on the ACF surface. Rather small clusters of TiO_2 crystals spread over the ACF surface with irregular shape, and the interstices among crystalline particles provide an ideal passageway for the transport and

adsorption of organic molecules such as AOII which molecular dimension is $1.24 \times 0.68 \times 0.22$ nm (Tamai et al., 1996). From the cross-sectional view of the TiO_2 film shown in Fig. 1f, the film thickness was estimated to be about 200 nm.

Fig. 2 shows the XRD spectra of the unmodified ACF and TiO_2/ACF . The peaks of TiO_2/ACF at 25.4° , 38.2° , 47.9° , 54.8° and 62.6° are related to the diffractions of the (101), (112), (200), (211), and (204) planes of anatase TiO_2 . No significant diffraction peaks of rutile-phase TiO_2 were detected in the XRD spectra. The broad peak at 43.4° of the unmodified ACF represents both the (100) and (101) planes of graphite. This typical peak still appears in the XRD spectra of TiO_2/ACF , which means that the microstructure of ACF is not altered upon the deposition of TiO_2 and the subsequent calcination at high temperature.

3.2. Cyclic voltammetry and electrochemical impedance spectroscopy analysis of TiO_2/ACF

Fig. 3 shows the cyclic voltammetry scans of sodium sulfate (0.01 M) solution without and with 200 mg/L of AOII, respectively, using the TiO_2/ACF electrode. An increase in anodic current was clearly observable under UV illumination compared to that under dark conditions. This can be attributed to the anodic bias applied to the TiO_2/ACF electrode, which provides a potential gradient across the TiO_2 film. The potential gradient can enhance the transport of photogenerated electrons on the TiO_2 film efficiently through the external circuit to the counter electrode, thus producing additional anodic photocurrent under UV light (Vinodgopal et al., 1993; Zaroni et al., 2003). Under UV irradiation, the photocurrent of the sodium sulfate (0.01 M) solution without AOII was higher than that of the same electrolyte with 200 mg/L of AOII. This is attributed to the UV light blockage by the orange color of AOII at high concentrations. Similarly, under dark conditions, the addition of 200 mg/L of AOII also created a slight drop in the anodic current, which could be caused by the adsorption of AOII onto the TiO_2/ACF surface. Adsorption of AOII on the photoanode may affect its electric conductivity to some extent. Moreover, the dark current in the sodium sulfate

Fig. 3 – Cyclic voltammetric scans of TiO_2/ACF in 0.01 M of sodium sulfate electrolyte with and without the presence of 200 mg/L of AOII under UV illumination and in dark (scan rate = 10 mV/s, scan range = 0.0–0.6 V vs. SCE).

reactive oxygen species (ROSS) cannot be formed without oxygen evolution, clearly there was no indirect electro-oxidation of AOII. With regard to the solution containing 200 mg/L of AOII without photoradiation, over the same bias range as above, neither oxidation nor reduction peaks were observed in the cyclic voltammogram. Furthermore, the anodic current was comparatively weak under the present experimental conditions. Therefore, direct electro-oxidation of AOII on the TiO_2/ACF electrode was not expected.

Time (min)	TiO_2/ACF , electro-photocatalysis (%)	TiO_2/ACF , photocatalysis (%)	TiO_2/ACF , electrochemical oxidation (%)	TiO_2/ACF , dark adsorption (%)	TiO_2/Ti , electro-photocatalysis (%)	Photolysis (%)
0	0	0	0	0	0	0
30	18	15	12	15	5	2
60	37	25	25	20	10	5
90	51	41	30	30	15	7
120	66	56	41	38	17	8
150	81	72	46	45	20	8
180	90	78	51	49	24	11

3.3. EPC degradation of AOII

For comparison, four other AOII removal processes, namely, photolysis, photocatalysis, electrochemical oxidation, and dark adsorption, in addition to EPC, were also tested. Fig. 5 and Table 1 show the results of the removal of AOII by the above processes. The adsorption experiment was conducted in dark without either electrical bias or photo-illumination. In EPC and electrochemical oxidation runs, the applied bias potential was kept constant at 0.5 V, whereas no electrical bias was applied to the TiO_2/ACF electrode in the PC oxidation experiments. It can be seen that the degradation of AOII by UV irradiation, i.e., photolysis, was not effective. The significant AOII removal by adsorption on TiO_2/ACF in dark could be attributed to its high specific surface area (S_{BET}) originating from the ACF support. However, with the filling of AOII in the

Processes	Photolysis	Dark adsorption (TiO ₂ /ACF)	Electrochemical oxidation (TiO ₂ /ACF)	PC ^a (TiO ₂ /ACF)	EPC ^b (TiO ₂ /ACF)	EPC ^b (TiO ₂ /Ti)
Removal percentage (%)	10.7	49.1	51.1	77.8	90.5	23.7

^a Photocatalysis.
^b Electro-photocatalysis.

Fig. 6 – UV-vis spectral changes as a function of reaction time during the EPC process on TiO_2/ACF . The initial concentration of AOII was 200 mg/L, the light source was 15 w UV_{254} lamp, and the electrical bias applied was 0.5 V.

micropores of ACF, it is expected that ACF will gradually lose its adsorption capacity. The degradation rate of AOII by electrochemical oxidation was almost parallel to that of adsorption, which implied that electrochemical oxidation did not contribute to the degradation of AOII at any significant level. The electro-photocatalysis, EPC, i.e., electrochemically assisted photocatalysis, rather than the combined process of electrochemical and photocatalytic oxidation, is the major process responsible for the degradation of AOII. Results shown in Fig. 5 clearly demonstrate that the EPC process using the TiO_2/ACF electrode yielded the best AOII degradation among all processes studied. AOII removal by EPC was much higher than that of photolysis, adsorption, and electrochemical oxidation.

The efficiency of heterogeneous reaction depends on the frequency and efficiency of collision between the catalyst

surface and the chemical species in the bulk solution (Kudo and Hiji, 1999). In the present EPC process, the three-dimensional TiO_2/ACF electrode offered a large contact surface area, and by virtue of strong adsorption, AOII molecules were concentrated in the TiO_2/ACF matrix. This would increase the transfer of localized AOII molecules toward the neighboring TiO_2 surface per the concentration gradient created therewith. At the interface between TiO_2 and ACF, AOII molecules reacted with the photogenerated oxidizing species and were decomposed readily (Yuan et al., 2005). Photodecomposition of adsorbed AOII molecules refreshed

Fig. 7 – The removal of TOC and AOII by EPC and by adsorption in dark using TiO_2/ACF . The initial concentration of AOII was 200 mg/L, the light source was 15 w UV_{254} lamp, and the electrical bias applied was 0.5 V.

Fig. 8 – The HPLC chromatogram of the AOII solution treated by the EPC process on TiO_2/ACF . The initial concentration of AOII was 50 mg/L, the light source was 15 w UV_{254} lamp, and electrical bias applied was 0.5 V.

the adsorption sites on the TiO_2/ACF matrix constantly, which allowed further adsorption of AOII and facilitated the electro-photocatalysis of AOII on the TiO_2 film (Fu et al., 2004). Likewise, in the PC process, the adsorption of AOII on the ACF support also improved the collision efficiency between AOII and the TiO_2 surface. In the absence of an electrical bias, the recombination rate of photogenerated electron-hole pairs was higher than that of the EPC process. As a result, the photodegradation rate of AOII by PC was lower than that by EPC. Up to 91% of AOII removal was observed using the EPC process, whereas the PC process only removed 78% of AOII under the same illumination period of 180 min. Moreover, large outer surface and good adsorption capacity for AOII, the 3D TiO_2/ACF exhibited much greater AOII degradation than the 2D TiO_2/Ti electrode.

Fig. 6 shows the UV-vis spectral changes of AOII solution during EPC treatment using the TiO_2/ACF electrode, with

the tautomeric profile of AOII illustrated in the inset. AOII has four absorption bands, with two in the visible region and two in the ultraviolet region. In the visible region, a major band at 484 nm and a shoulder band at 430 nm due to the hydrazone and the azo form of AOII, respectively, were observed. The other two bands, at 230 and 310 nm in the ultraviolet region, are attributed to the benzene and the naphthalene rings of the dye, respectively (Wu et al., 2000; Styliadi et al., 2003). All four absorption bands diminished steadily with increase in reaction time, which indicated that the four characteristic structures of the dye molecule were photodegraded simultaneously.

In any advanced chemical oxidation system such as EPC, it is important to know both the degree of the decomposition of the parent compound and that of mineralization. In this study, the degree of mineralization was measured in terms of the change of TOC. Fig. 7 shows the percentage of TOC removal

Fig. 9—Conceptual presentation of the degradation of AOII by EPC over the TiO_2/ACF surface.

with respect to reaction time by EPC and by adsorption in dark using TiO_2/ACF . According to Fig. 7, the extent of AOII removal by adsorption in dark was similar to that of TOC removal. Since no AOII decomposition took place, the amount of AOII adsorbed onto TiO_2/ACF was the same as that of TOC removed. A major difference can be seen by comparing the percentage of AOII removal with that of TOC removal by the EPC process. The degree of mineralization was lower than that of the decomposition of AOII, which is not uncommon in heterogeneous catalysis (Fernandes et al., 2004; Li et al., 2006; Murugananthan et al., 2007). The cleavage of the AOII molecular structure first occurs at positions that are susceptible to free radical attack with the production of various intermediates. This step is followed by further radical attack of the intermediates to yield CO_2 and oxyanions such as nitrate and sulfate. Although the percent TOC removal by EPC was close to that of adsorption in dark, the organic components contributing to TOC in these two solutions were different. In the adsorption system, TOC was contributed totally from the original dye, i.e., AOII, present, whereas in the EPC system, in addition to the residual AOII per se, the organic intermediates evolved from the electro-photocatalytic degradation of AOII contributed to TOC as well. Moreover, the degree of mineralization by the EPC system exceeded that of adsorption in dark at time greater than 120 min.

In order to better understand EPC degradation using TiO_2/ACF , the decay of AOII and the evolution of intermediates were followed by HPLC measurements. Fig. 8 shows the chromatogram of the AOII treated by the EPC at various time periods. Based on the well-developed (major) peak at the retention time of 9.7 min, which is correspondent to the parent compound, it is seen that AOII underwent remarkably efficient degradation by EPC using the TiO_2/ACF electrode, achieving 95% removal within the first 120 min. Concomitant with the decomposition of AOII, a group of intermediates with retention time around 6 min were detected. These intermediates appeared during the first few hours; after reaching the peak values at about 120 min, the peaks diminished along with AOII as the reaction time was extended. The inset of Fig. 8 shows clearly that these intermediates might also be present in the original AOII solution in comparatively small amounts. This could be that the intermediates detected by HPLC happened to be the minor organic impurities of the AOII used, too. Nonetheless, the impurities and newly formed intermediates were both degraded by the electro-photocatalytic TiO_2/ACF . After 240 min of photoradiation, the concentration of the intermediates was insignificant.

Fig. 9 presents the conceptual reaction pathway of the electro-photocatalytic degradation of AOII over TiO_2/ACF . First, AOII molecules diffused to the vicinity of the TiO_2/ACF surface and became absorbed into the micropores of ACF. The adsorbed dye molecules subsequently were transferred by surface diffusion to the interface between TiO_2 and ACF, where photodegradation took place to yield intermediates. A fraction of the intermediates continued to be adsorbed on the TiO_2/ACF surface and underwent photodecomposition until they were mineralized to CO_2 or other inorganic ions, whereas some of the intermediates went through a desorption-adsorption process until they became totally mineralized. In addition, the recombination of the photoinduced electron-

hole pairs was suppressed efficiently by applying an external electric field. The electrons were transferred to the cathode through the external circuit, and the remaining active holes could oxidize the organics or react with H_2O and OH^- to form OH radicals. It is known that $\cdot\text{OH}$ radicals are strong oxidants that react with organic or inorganic compounds without selectivity.

4. Conclusions

A coherent TiO_2 film of the anatase type was deposited successfully on activated carbon fibers by liquid phase deposition (LPD) method followed by calcination at 350 °C in nitrogen atmosphere. The microstructure and surface properties of ACF remained intact during the deposition process. An enhanced photocatalytic degradation of AOII was achieved by applying a 0.5-V bias across the TiO_2/ACF electrode under UV illumination, which is known as the electro-photocatalytic (EPC) process. In the EPC process, the applied bias was not intended to create electrochemical oxidation of AOII because the potential applied was relatively low, which could generate only a weak anodic current. The applied bias was low but was sufficiently high enough to inhibit the recombination of holes and electrons efficiently and promoted AOII degradation as confirmed by EIS measurements. Additionally, the three-dimensional TiO_2/ACF electrode has large outer surface area along with good adsorption capacity for organic compounds, which improved the contact efficiency between the organic contaminants in question and the TiO_2 surface and ultimately enhanced the EPC activity. Over a reaction time of 180 min, it is possible to remove 91% of AOII at an initial concentration of 200 mg/L; the percent AOII removal was 95% in 120 min when the initial concentration was 50 mg/, however. Moreover, large outer surface and good adsorption capacity for AOII, the 3D TiO_2/ACF exhibited much greater AOII degradation than the 2D TiO_2/Ti electrode. A group of intermediates sensitive to HPLC analysis during the EPC decomposition of AOII was detected. The intermediates reached peak production in about 120 min, and then decreased upon further increase in reaction time.

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